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**PATENT KANTOOR
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EN NYWERHEID**



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Certificate

REPUBLIC OF SOUTH AFRICA

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the documents attached hereto are true copies of the Forms P2, P6,
provisional specification and drawings of South African Patent
Application No. 2003/1938 in the name of SASOL TECHNOLOGY
(PROPRIETARY) LIMITED

Filed : 10 March 2003
Entitled : Production of Linear Alky
Benzene

Geteken te **PRETORIA** in die Republiek van Suid-Afrika, hierdie **16th** dag van **March 2004**
Signed at **in the Republic of South Africa, this** **day of**

dag van
16th . . . March 2004
day of

Registrar of Patents

PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

| REPUBLIC OF SOUTH AFRICA | | | REGISTER OF PATENTS | | | PATENTS ACT, 1978 | | |
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| FULL NAME(S) OF APPLICANT(S)/PATENTEE(S) | | | | | | | | |
| 71 | SASOL TECHNOLOGY (PROPRIETARY) LIMITED | | | | | | | |
| APPLICANTS SUBSTITUTED: | | | | | | DATE REGISTERED | | |
| 71 | | | | | | | | |
| ASSIGNEE(S) | | | | | | DATE REGISTERED | | |
| 71 | | | | | | | | |
| FULL NAME(S) OF INVENTOR(S) | | | | | | | | |
| 72 | 1. GREAGER, IVAN 2. JANSEN, WILHELMINA 3. DE WET, JOHAN PIETER 4. SCHOLTZ, JAN HENDRIK 5. DESMET, MIEKE ANN | | | | | | | |
| PRIORITY CLAIMED | | COUNTRY | | NUMBER | | DATE | | |
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| 54 | PRODUCTION OF LINEAR ALKYL BENZENE | | | | | | | |
| ADDRESS OF APPLICANT(S)/PATENTEE(S) | | | | | | | | |
| 1 STURDEE AVENUE, ROSEBANK, 2196, GAUTENG, SOUTH AFRICA | | | | | | | | |
| ADDRESS FOR SERVICE | | | | | | S & F REF | | |
| 74 | SPOOR & FISHER, SANDTON | | | | | | PA134800/P | |
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APPLICATION FOR A PATENT
AND ACKNOWLEDGEMENT OF RECEIPT 03.03
(Section 30 (1) – Regulation 22)

R 00600.0

The granting of a patent is hereby requested by the undermentioned applicant on the basis of the present application filed in duplicate.

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21 01

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FULL NAME(S) OF APPLICANT(S)

71

SASOL TECHNOLOGY (PROPRIETARY) LIMITED

CORRECTIONS
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ADDRESS(ES) OF APPLICANT(S)

1 KLASIE HAVENGA ROAD, SASOLBURG, 1947, FREE STATE, SOUTH AFRICA
1 STURDEE AVENUE, ROSEBANK, 2196, GP, S.A.

TITLE OF INVENTION

54

PRODUCTION OF LINEAR ALKYL BENZENE

THE APPLICANT CLAIMS PRIORITY AS SET OUT ON THE ACCOMPANYING FORM P.2. THE EARLIEST PRIORITY CLAIM IS:

COUNTRY: NIL

NUMBER: NIL

DATE: NIL

THIS APPLICATION IS FOR A PATENT OF ADDITION TO PATENT APPLICATION NO.

21 01

THIS APPLICATION IS A FRESH APPLICATION IN TERMS OF SECTION 37 AND IS BASED ON APPLICATION NO.

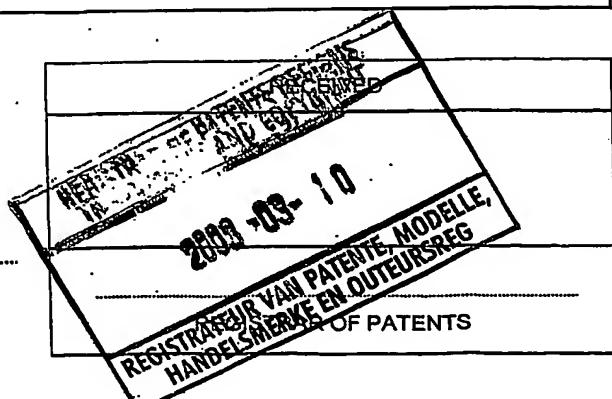
21 01

THIS APPLICATION IS ACCCOMPANIED BY:

- 1. A single copy of a provisional specification of 11 pages.
- 2. Drawings of 2 sheets.
- 3. Publication particulars and abstract (Form P.8 in duplicate).
- 4. A copy of Figure of the drawings (if any) for the abstract.
- 5. Assignment of invention.
- 6. Certified priority document.
- 7. Translation of the priority document.
- 8. Assignment of priority rights.
- 9. A copy of the Form P.2 and the specification of S.A. Patent Application No .
- 10. Declaration and power of attorney on Form P.3.
- 11. Request for ante-dating on Form P.4.
- 12. Request for classification on Form P.9.
- 13. Form P.2 in duplicate.
- 14. Other.

74 ADDRESS FOR SERVICE: SPOOR & FISHER, SANDTON

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SPOOR & FISHER
PATENT ATTORNEYS FOR THE APPLICANT(S)

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PROVISIONAL SPECIFICATION

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FULL NAMES OF APPLICANTS

71 SASOL TECHNOLOGY (PROPRIETARY) LIMITED

FULL NAMES OF INVENTORS

72 GREAGER, IVAN
JANSEN, WILHELMINA
DE WET, JOHAN PIETER
SCHOLTZ, JAN HENDRIK
DESMET, MIEKE ANN

TITLE OF INVENTION

54 PRODUCTION OF LINEAR ALKYL BENZENE

PRODUCTION OF LINEAR ALKYL BENZENE

BACKGROUND OF THE INVENTION

THIS invention relates to a method for producing linear alkyl benzene.

Alkyl benzene derivatives, such as alkyl benzene sulphonates, are among others, used in detergent and surfactant product applications. Environmental legislation requires that these products are biodegradable. It is well known that, to be bio-degradable, it is important for the alkyl chain to be linear, i.e. with very little or no branching and low, if any, quaternary carbons.

In conventional processes for producing linear alkyl benzenes, a hydrocarbon stream is hydrogenated in order to convert oxygenates and olefin species in the stream to paraffins. Hydrogenation also allows for the removal of sulphur and nitrogen contaminants that may be present. Following the hydrogenation reaction, the resulting paraffin stream is fractionated into various carbon ranges. A carbon range, for example the C₈ to C₁₆ range, which includes branched paraffins, is passed through a molecular sieve. The branched paraffins are rejected as a raffinate stream, whilst the linear paraffins are passed through a dehydrogenation reactor to form an olefin/paraffin mixture. This mixture is then fed to an alkylation plant and reacted with benzene to form linear alkyl benzene (LAB). The linear alkyl benzene is then sulphonated to form linear alkyl benzene sulphonates (LAS). A problem with this approach is the relatively high cost of paraffinic starting material and the high cost associated with the production of linear paraffins from kerosene feedstocks.

United Kingdom Patent No. 669,313 in the name of California Research Corporation, United States Patent No. 3,674,885 in the name of Atlantic Richfield Company and International Patent Publication No. WO 01/64610 in the name of Chevron USA Inc. disclose the use of a hydrocarbon condensate from the Fischer-Tropsch process, in the production of alkyl benzene. These references disclose that the hydrocarbon condensate contains olefins that are used in the alkylation reaction to form linear alkyl benzene. These references are limited to the use of "high temperature" Fischer-Tropsch processes wherein the Fischer-Tropsch reaction is carried out temperatures of approximately 300°C and higher, and the preferred catalysts are iron-containing catalysts, for the production of the hydrocarbon condensate. The high temperature Fischer-Tropsch processes were found to be suitable because the hydrocarbon condensate contains a high concentration of olefins, usually in the region of around 70%. Although these references refer to linear olefins obtained from a high temperature Fischer Tropsch process in practice the olefins exhibit more than 10% branching.

SUMMARY OF THE INVENTION

According to the invention there is provided a method for producing linear alkyl benzene, the method including the steps of obtaining a hydrocarbon condensate containing olefins and paraffins from a low temperature Fischer-Tropsch reaction;

- a) fractionating a desired carbon number distribution from the hydrocarbon condensate to form a fractionated hydrocarbon condensate;
- b) extracting oxygenates from the fractionated hydrocarbon condensate;
- c) combining the hydrocarbon condensate with the feed stream from step (g) to form a combined stream;

- d) alkylating olefins in the combined stream with benzene in the presence of a suitable alkylation catalyst in an alkylation reactor;
- e) recovering linear alkyl benzene from the alkylation reactor;
- f) recovering unreacted paraffins from the alkylation reactor;
- g) dehydrogenating the unreacted paraffins in the presence of a suitable dehydrogenation catalyst to form a feed stream containing olefins and paraffins; and
- h) sending the feed stream containing olefins and paraffins to step (c).

Typically, the low temperature Fischer-Tropsch reaction is carried in a slurry bed reactor at a temperature of 160°C - 280°C, preferably 210°C - 260°C, and in the presence of a cobalt catalyst to provide a hydrocarbon condensate containing 60 to 80% by weight paraffins and 10 to 30% by weight, typically less than 25% by weight, olefins. The olefins having a linearity of greater than 92%, preferably greater than 95%.

The oxygenates may be extracted by distillation, dehydration or liquid-liquid extraction, preferably liquid-liquid extraction. A light solvent such as dry methanol or a mixture of methanol and water, is preferably used in the liquid-liquid extraction.

Typically, the dehydrogenation reaction at step (g) is carried out at a conversion rate of 10%-15%.

Generally, the fractionated hydrocarbon condensate from step (b) will have a olefin concentration of from 15% to 30% by weight, the feed stream from step (g) will have an olefin concentration of 10% to 15% by weight, and the combined stream at step (c) will have an olefin concentration of 12.5% to 22.5% by weight.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a block diagram of a process according to the invention for producing linear alkyl benzene; and

Figure 2 is a block diagram of a process for extracting oxygenates from a hydrocarbon product, used in the process of Figure 1.

DESCRIPTION OF PREFERRED EMBODIMENTS

This invention relates to the use of a hydrocarbon condensate stream from a low temperature Fischer-Tropsch reaction in the production of linear alkyl benzene.

In the Fischer-Tropsch process, synthesis gas (carbon monoxide and hydrogen), obtained from gasification of coal or reforming of natural gas, is reacted over a Fischer-Tropsch catalyst to produce a mixture of hydrocarbons ranging from methane to waxes and smaller amounts of oxygenates.

In a low temperature Fischer-Tropsch reaction, the reaction takes place in a slurry bed reactor or fixed bed reactor, preferably a slurry bed reactor, at a temperature in the range of 160°C - 280°C, preferably 210°C - 260°C, and a pressure in the range of 18-50 bar, preferably between 20-30 bar, in the presence of a catalyst. The catalyst may include iron, cobalt, nickel or ruthenium. However, a cobalt-based catalyst is preferred for the low temperature reaction. Usually, the cobalt catalyst is supported on an alumina support.

During the Fischer-Tropsch reaction, a lighter hydrocarbon vapour phase is separated from a liquid phase comprising heavier liquid hydrocarbon products. The heavier liquid hydrocarbon product (waxy products) is the

major product of the reaction and may, for example, be hydrocracked to produce diesel and naphtha.

The lighter hydrocarbon vapour phase which comprises gaseous hydrocarbon products, unreacted synthesis gas and water is condensed to provide a "condensation product" which comprises an aqueous phase and a hydrocarbon condensation product phase.

The hydrocarbon condensation product includes olefins and paraffins in the C₄ to C₂₆ range, and oxygenates including alcohols, esters, aldehydes, ketones and acids.

Olefins, which are predominantly alpha olefins, only make up approximately 15 to 30%, by weight, of the hydrocarbon condensation product. Generally, this product would not be considered useful in an alkylation reaction to form linear alkyl benzene, because of the low concentration of olefins. However, it has been found that the olefins have a very high degree of linearity of greater than 95% and, even though they only make up 15 to 30%, by weight of the hydrocarbon condensate product, it is an excellent feed for the production of linear alkyl benzene and provides an economically advantageous manner for the production of highly linear alkyl benzene. The paraffins in the hydrocarbon condensate product also have a high degree of linearity. These paraffins do not react in the alkylation reaction and are recovered as a high quality paraffin product which is dehydrogenated and recycled to the alkylation reaction. The feed stream from the dehydrogenation process has a relatively low olefin concentration (10% - 15% by weight), and the combination of this feed stream with hydrocarbon condensate from the low temperature Fischer-Tropsch reaction increases the olefin concentration in the combined feed provided to the alkylation reaction due to the higher olefin concentration in the hydrocarbon condensate from the low temperature Fischer-Tropsch reaction. This results in a reduction in the recycle flow rate which leads to savings in both capital expenditure and operation expenditure.

Referring to Figure 1, by way of example, a hydrocarbon condensation product 10 from a low temperature Fischer-Tropsch reaction contains 20% by weight olefins, 74% by weight paraffins, and 6% by weight oxygenates. The hydrocarbon condensation product 10 is passed through a fractionation column 12 and a C₁₀-C₁₃ cut 14 is separated therefrom. The cut 14 contains 22% by weight olefins, 71% by weight paraffins and 7% by weight oxygenates. The cut 14 is then sent to a oxygenate removal unit 16 where the oxygenates 18 are removed to provide a hydrocarbon feed stream 24 containing 23% by weight olefins and 77% by weight paraffins and less than 0.01% by weight oxygenates.

As mentioned above, the olefin concentration in the cut 14 is low. It is therefore desirable to use an oxygenate removal step which preserves the olefin concentration. In the prior art, many methods of extracting oxygenates from hydrocarbon streams are suggested. Such removal methods include hydrogenation, azeotropic distillation, extractive distillation, vapour phase dehydration, liquid phase dehydration and liquid-liquid extraction. It has been found that distillation, liquid-liquid extraction and dehydration processes are preferred as they tend to preserve the olefin concentration.

With reference to figure 2, a liquid-liquid extraction process of the invention includes an extraction column 20. The cut 14 from Figure 1 is fed into the extraction column 20 at or near the bottom thereof and a solvent stream 21 is fed into the extraction column 20 at or near the top thereof.

Raffinate 22 from the top of the extraction column 20, which includes olefins and paraffins and a small amount of solvent, enters a raffinate stripper column 23 and a hydrocarbon feed stream containing olefins (23% by weight), and paraffins (77% by weight) and less than 0.01% by weight oxygenates exits as a bottoms product 24 while solvent exits as a tops product 25 and is returned to the solvent feed stream 21. If it is desired to recover the bottoms product 24 as a vapour stream, this can be done by

adding a vapour side draw to the column just above the reboiler. The liquid product from the reboiler will then be a very small effluent stream.

An extract 26 is drawn from the bottom of the extraction column 20 and is fed to solvent recovery column 27. Oxygenates exit as a bottoms product 28 from the solvent recovery column 27, while solvent exits as a tops product 29 and is recycled to the solvent stream 21. The oxygenate content of the tops product 29 can be as low as 50 ppm, depending on the solvent to feed ratio used in the extraction column 20.

The solvent 21 can be any polar material that has partial miscibility with the feed stream 14, such as tri-ethanol amine, tri-ethylene glycol with between zero and 20% water, acetonitrile with between 5% and 20% water, acetol, diols, methanol, or ethanol and water. A combination of the above solvents is also possible.

Normally, a high-boiling solvent is preferred for liquid-liquid extraction because the solvent recovery steps after extraction requires less energy than will be the case for a low-boiling solvent. However, it has been found that dry methanol, or a mixture of methanol and water, which is a low-boiling solvent, need not suffer from this drawback, because it can be effective at low solvent to feed ratios (this can be lower than 1:1 if the required oxygenate removal is not too severe).

A study of the different azeotropes that exist between components in the feed and methanol and water would lead one to expect that it would not be possible to distil water overhead in the solvent recovery column 27 without azeotroping oxygenates overhead as well. Surprisingly, this turns out not to be the case. Methanol, which does not form azeotropes with any of the other species present, prevents the water/oxygenate azeotropes from distilling over at the same temperature as the paraffins and olefins. This appears to be due to an extractive distillation effect. Additionally, it is possible to distil the paraffins and olefins overhead, while recovering all the oxygenates as bottom products (this is not possible for a dry methanol

system, because only a fraction of the paraffins and olefins can be distilled overhead without carrying over oxygenates in a dry methanol system). This has the effect of enhancing the overall paraffin and olefin recovery of the process, because the overheads 29 of the solvent recovery column 27 is recirculated to the extraction column 20, which means that the paraffins and olefins will be forced to leave the process in the product stream 24. It is therefore possible to have a pure hydrocarbon (paraffin and olefin) stream 24, and a pure oxygenate and water stream 28 as products from the process, without the use of a countersolvent in the extraction column. In this mode of operation, all the methanol, and part of the water (10-50%) are also recovered in the overhead stream 29.

Because the bottoms product 28 contains a high percentage of water (10-60%), this stream will form two liquid phases that can be decanted in a decanter 30. The organic phase will be a pure oxygenate stream 31, which leaves the process as a product. The aqueous phase will be a stream 32, which can be recycled to the extraction column 20. This stream can either enter the extraction column at the top along with the solvent stream 21, or slightly lower down the column 20, to prevent the low amount of oxygenates that will be present in this stream from appearing in the raffinate stream 22.

It is also possible to run the extraction column 20 and the solvent recovery column 27 at different methanol / water ratios. This may be desirable because a high water content in the extraction column 20 will lead to increased solvent to feed ratios (because of reduced solubility of oxygenates in the solvent), while a certain amount of water is necessary to achieve the extractive distillation effect in combination with methanol to recover all the paraffins and olefins as overhead products in the solvent recovery column 27. The different methanol / water ratios in the two columns (20 and 27) can be achieved by diverting some of the water in stream 32 to stream 26 by means of a stream 33.

Referring back to Figure 1, according to the invention the liquid hydrocarbon product 24 from the oxygenate removal process 16 is supplied to an alkylation/dehydrogenation circuit indicated generally by the numeral 40. The alkylation/dehydrogenation circuit 40 includes an alkylation reactor 42 and a dehydrogenation process 44. An alkylation reaction in the alkylation reactor 42 may be carried out by using a Friedel-Crafts type condensation catalyst such as AlCl_3 , H_2SO_4 , BF_3 , HF or a solid acid catalyst. In the present case, the UOP DETAL solid acid catalyst alkylation technology is used. Typically, the alkylation reaction is carried out at a temperature of approximately 100°C and a pressure of about 300kPa (abs), in the presence of UOP's proprietary DETAL catalyst (see Smith R. (1991) Linear alkylbenzene by heterogeneous catalysis. PEP Review No. 90-2-4, SRI International).

After alkylation, the unreacted benzene is recovered and recycled to the alkylation reactor 42. The paraffins are recovered and are sent to the dehydrogenation process 44. In the present case, the UOP Pacol dehydrogenation technology is used for activation of the paraffins. Typically, the dehydrogenation reaction is carried out at 400-500°C and 300kPa (abs), in the presence of a modified platinum catalyst on an aluminium oxide substrate. Conversion of paraffins to olefins is limited to 10-15% in order to limit further dehydrogenation of mono-olefins to dienes and cyclools. UOP's DEFINE and PEP processes are used to further remove unwanted by-products from the pacolate, that are formed during dehydrogenation. The DEFINE process selectively hydrogenates dienes to the mono-olefins, whilst PEP removes cyclic compounds from the pacolate.

With reference to the alkylation/dehydrogenation circuit 40, an olefin-paraffin feed 46 is introduced into the alkylation reactor 42 which is also supplied with benzene 48. The olefins from the olefin paraffin feed 46 react with the benzene 48 in the alkylation reactor 42 to provide linear alkylbenzene 50, unreacted paraffins 52 and unreacted benzene 54. The unreacted benzene 54 is recycled to the alkylation reactor. The unreacted paraffin 52 is recovered and sent to the dehydrogenation process 44 to

produce a paraffin olefin mixture 46A which is supplied to the paraffin olefin line 46, and hydrogen 54.

The paraffins 52 leaving the alkylation reactor 42 are of a high quality and comprise substantially 100% paraffin. In this example, the dehydrogenation process 44 operates at a paraffin conversion of 12% and the paraffin olefin mixture 46A leaving the dehydrogenator 44 has a olefin concentration of 12% and a paraffin concentration of 88%. The hydrocarbon product 28 is introduced mid-way along to the paraffin olefin stream 46. In this example, the hydrocarbon product 24 has an olefin concentration of 23% and a paraffin concentration of 77% and, on mixing with the paraffins and olefins from 46A, form an olefin-paraffin feed stream 46B with an olefin concentration of 13.5% and a paraffin concentration of 86.5%. This increase in olefin concentration in the olefin-paraffin feed stream 46 results in a reduction in the recycle flow rate through the dehydrogenation process 44 and alkylation reactor 42, for a fixed production of linear alkyl benzene. Thus, an increased olefin concentration in the olefin-paraffin feed 46 translates into potential savings in both capital expenditure and operation expenditure. From a capital expenditure perspective, the reduced recycle flow rate allows for a reduction in the size of the dehydrogenation reactor in the dehydrogenation process 44 as well as a reduction in size of the alkylation reactor 42, for a fixed residence time and the reduced paraffin flow rate will allow for a reduction in the size of the paraffin recovery column and ancillary equipment. The operation expenditure savings include a reduced mass flow rate through the dehydrogenation reactor 44 and results in a reduction in the required hydrogen flow rate required for selective hydrogenation of dienes and reduction in the paraffin flow rate will allow for savings in utilities such cooling water, steam (or hot oil) and electricity.

In a final step of the process, the highly linear alkyl benzene 44 is introduced to a sulphonate reactor 52 and sulphonated using sulphuric acid, oleum or sulphur trioxide. Sulphur trioxide is currently the preferred

process. The sulphonation process results in the formation of a highly linear alkylbenzene sulphonates.

The process of the invention makes use of a feed stream in the form of a condensate product from a low temperature Fischer-Tropsch reaction which would not be expected feasible for producing linear alkyl benzene. The process produces a desirable highly linear alkyl benzene product, while at the same time produces a high quality paraffin product which is dehydrogenated and recycled to the alkylation reaction. The feed stream from the dehydrogenation process has a relatively low olefin concentration (10% - 15% by weight), and the combination of this feed stream with hydrocarbon condensate from the low temperature Fischer-Tropsch reaction increases the olefin concentration in the combined feed provided to the alkylation reactor which results in savings in both capital expenditure and operation expenditure.

Dated this 10TH day of March 2003



Spoor & Fisher
Applicant's Patent Attorneys

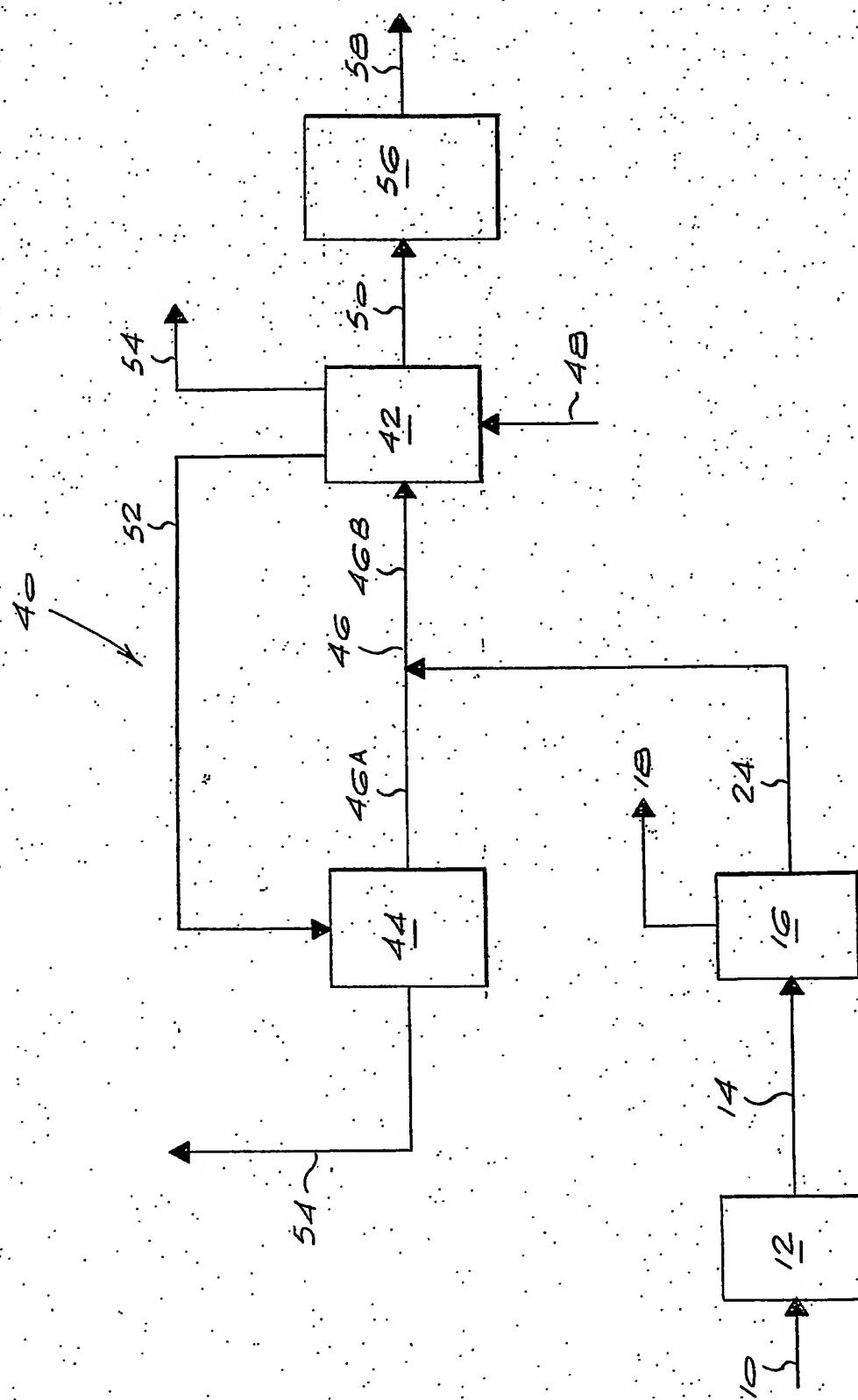


Fig.1

Fig.2

